Synthesis and Electrochemical Characterization of PdCo/MWCNT towards Formic Acid Fuel Cells

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Introduction

A growing global population, the technological advances being made, and the greater push towards greener energy bring a great need for alternative sources of energy. In order to keep up with ever increasing demands for energy, direct formic acid fuel cells (DFAFCs) show great promise. However, the need for a cost effective, robust and efficient anodic catalyst towards DFAFCs is still imminent. Therefore, this study aims to investigate the efficiency, conductivity, and stability of palladium and cobalt binary nanocomposites on multiwalled carbon nanotubes (MWCNTs) substrate. Three nanocomposites were synthesized with varying amounts of cobalt (0%, 10% and 15%) and a fixed amount of palladium (20%) on MWCNTs using a simple one pot synthesis utilizing sodium borohydride as a reducing agent. This allowed the palladium and cobalt nanoparticles to disperse along the carbon nanotube surface to provide greater catalytic surface area. The morphology was characterized by scanning electron microscopy (SEM) imaging technique showing the binary nanocomposites were dispersed along the carbon nanotube surface. Cyclic voltammetry (CV) was then employed for the electrochemical characterization of formic acid oxidation (FAO) using the nanocomposites in a 0.50 M HCOOH with 0.10 M H_2SO_4 electrolyte. A glassy carbon working electrode (GCE) was modified with a fixed amount of the nanocomposites (0.025 mg/cm^2 GCE) to enable correct comparisons of the catalytic effect of various amounts of cobalt. The nanocomposites have demonstrated the direct formic acid oxidation pathway facilitated by a bifunctional effect. This along with all other electrochemical data was compared to a standard commercially available 20% palladium on carbon Pearlman catalyst.

Formic Acid Electrooxidation Pathway

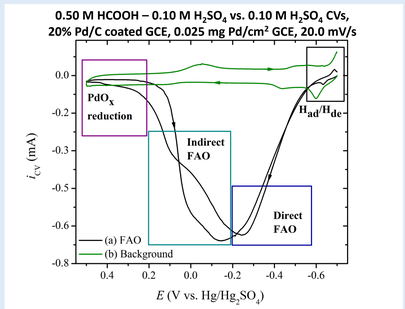


Figure 1. Typical formic acid electrooxidation pathways.

Nanocomposite Syntheses

Table 1. Masses of $CoCl_2 \cdot 6H_2O$, $PdCl_2$, and MWCNT

	0%	10%	15%
Cobalt (II) Chloride Hexahydrate	0 mg	24.234 mg	36.351 mg
Palladium (II) Chloride	20 mg	20 mg	20 mg
MWCNT	60 mg	60 mg	60 mg

Varying amounts of weight to weight percentages of $CoCl_2 \cdot 6H_2O$ were calculated and combined with fixed amounts of $PdCl_2$ and MWCNT.

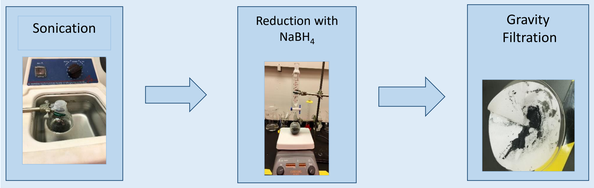
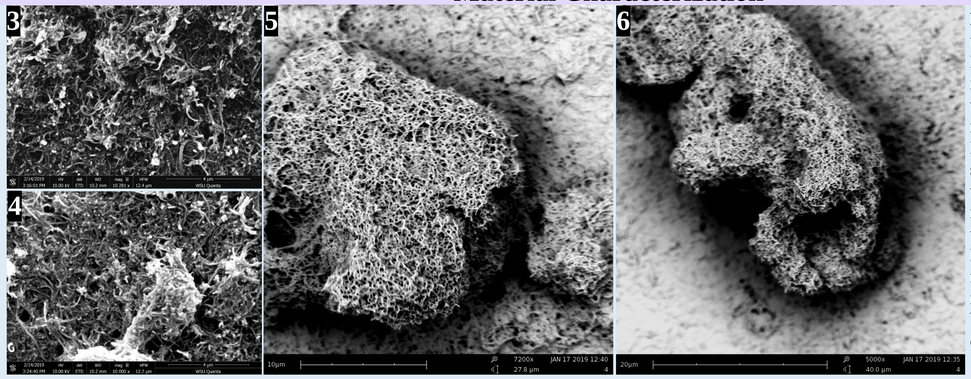


Figure 2. A one pot synthesis scheme to prepare the mono and binary nanocatalysts.

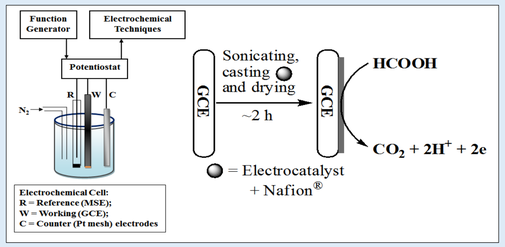
Material Characterization

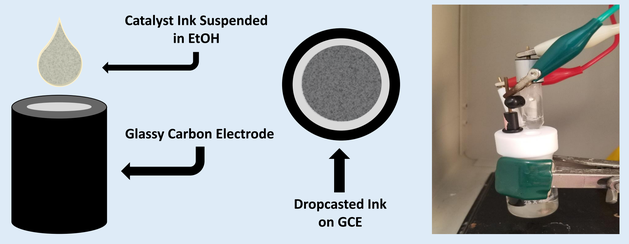


Figures 3-6 were obtained by using Scanning Electron Microscopy (SEM). These images were used to determine the morphology of the nanocomposites. The use of MWCNT offer a large amount of surface area. It can be assumed that the palladium and cobalt nanoparticles are spread throughout the surface of the MWCNT. Although the size does not allow for full visibility of the nanoparticles, their presence may be supported through electrochemical analysis.

Figures 3-6. Morphology of PdCo/MWCNT surface.

Electrode Modification and Cyclic Voltammetry Setup





Figures 7, 8 & 9. Electrode Modification Scheme and Setup for Cyclic Voltammetry (CV). These figures show the process of dropcasting and sealing catalyst ink on the glassy carbon working electrode (GCE) using Nafion®. CV was collected using the modified GCE (working), a Pt wire counter electrode, and a Hg/Hg_2SO_4 (Satd. K_2SO_4) (MSE) reference electrode in a 0.5 M HCOOH – 0.1 M H_2SO_4 electrolyte solution at a 20 mV/s scanning rate.

Electrochemical Results

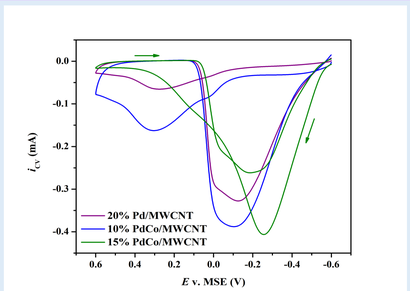


Figure 10. 1st sweep segment using the prepared mono and binary nanocatalysts shows enhanced direct FAO activity.

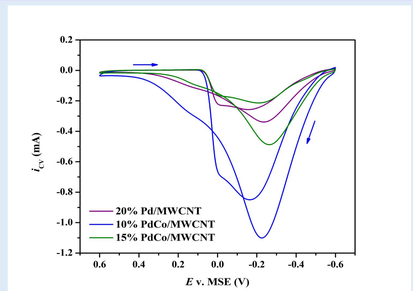


Figure 11. 25th sweep segments to demonstrate stability of the prepared materals towards FAO.

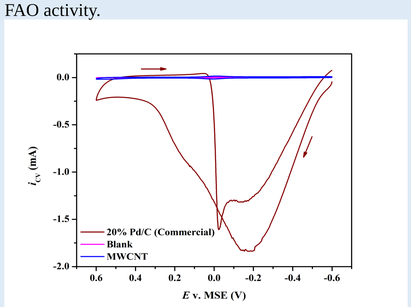


Figure 12. Commercial standard v. controlled blanks.

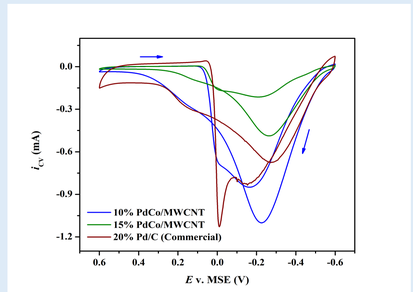


Figure 13. 25th sweep of the binary v. commercial nanocatalysts.

In Figure 10, the first sweep of the three experimental nanocatalysts shows that all three samples follow the FAO pathway. Among the three, it is clear that the addition of cobalt does allow for a greater peak shift towards the negative voltage direction that explains the enhanced direct FAO. In this segment the 10% and 15% nanocatalysts are in very close range to each other with the 15% falling closer to the direct FAO pathway. Figure 11 shows the 25th sweep segment which shows that in terms of efficiency throughout lifespan, the 10% has more durability even shifting towards the direct FAO pathway over time. In Figure 12, the commercial standard is shown against a blank run and a run with only the MWCNT showing the importance of the addition of the metals for catabolic activity. Figure 13 is a comparison of the highest performing experimental samples of the 10% and 15% nanocatalyst against the commercial standard at the 25th sweep. The 10% sample keeps up with the commercial standard very well showing very similar results. The 10% also shows exceptional performance in that it may carry more current than the commercial standard after prolonged cycling while still remaining in the direct FAO pathway. All CV's were collected with a constant catalytic load of 0.025 mg/cm^2 of GCE.

Discussion

This study demonstrates the advantages of using MWCNT as a carbon base for the FAO catalysts. This carbon base offers a very high surface area which is advantageous for the wide dispersal of transition metals on its surface (Figures 3-6). The importance of transition metals as catalysts was also noted in the result of the cyclic voltammogram of only the MWCNT sample (Figure 12). The binary metal system showed very promising results in terms of catalytic activity, efficiency, and stability over time. In comparison to the commercial standard (Figure 13), it does appear that the addition of cobalt may help increase stability over time as well as serving as an aide to maintain the use of the direct FAO pathway. The use of a binary metal system shows great potential for application as an efficient, stable, and cost-effective anodic catalysts towards formic acid fuel cells. However, further research is necessary to confidently conclude the effects of different ratios of the PdCo binary system.

Conclusion

- Pd and PdCo nanocatalysts were prepared utilizing a simple one pot synthesis on MWCNT support.
- MWCNT provide a large surface area for the dispersion of metal nanoparticles as revealed by the SEM images.
- CV shows that PdCo binary nanocomposites can facilitate the direct FAO pathway.
- PdCo binary system may provide stability and durability over time.

Future Work

Further studies may include variations in the w/w percentage of Pd/Co as well as the use of other abundant transition metals. Different diameter of MWCNT may also use to vary morphology and surface area available for dispersion.

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